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Diagenetic Oxygen Equivalents Model of Sediment Oxygen Demand

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A DIAGENETIC OXYGEN EQUIVALENTS MODEL OF SEDIMENT OXYGEN DEMAND

by

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16. ABSTRACT

The consumption of oxygen in the overlying water by sediments is an important component in the oxygen balance of most natural waters. Conventional practice is to specify the magnitude of this sink using direct uptake measurements. Unfortunately, if the management alternative being investigated affects the supply of particulate organic material to the sediment then the use of the existing sediment oxygen demand (SOD) for dissolved oxygen projections may be in error. In general the evaluation of the control of point and non-point sources which contribute to, or affect the flux of particulate organic matter to the sediments require a model of sediment oxygen demand.

It is the purpose of this paper to present a model of sediment oxygen demand which attempts to solve the problem in a fashion which ultimately dispenses with the complexity and relates sediment oxygen demand to the flux of the oxygen equivalents of all reduced substances in the interstitial water without specific regard to their identity.

The oxygen equivalents model of SOD provides a simple, comprehensive framework within which to understand the phenomena of SOD.

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Introduction

The consumption of oxygen in the overlying water by sediments is an important component in the oxygen balance of most natural waters. Conventional practice is to specify the magnitude of this sink using direct uptake measurements. Unfortunately, if the management alternative being investigated affects the supply of particulate organic material to the sediment then the use of the existing sediment oxygen demand (SOD) for dissolved oxygen projections may be in error. Examples include the oxygen consequences of phosphorus loading reductions where algal carbon decay in the sediment is a principle DO sink. In general the evaluation of the control of point and non-point sources which contribute to, or affect the flux of particulate organic matter to the sediments require a model of sediment oxygen demand.

At first glance, this task appears to be quite complicated since both aerobic and anaerobic reactions in sediments are involved. Biologically mediated reactions (e.g. methane production and consumption) as well as inorganic reactions (e.g., sulfide oxidation) are all candidates for consideration. Layered models which distinguish zones of oxygen consumption and nitrate reduction (Vanderborght and Billen, 1975; Jahnke et al., 1982) and a three layer model including methane formation (Klapwijk and Snodgrass, 1983) have been proposed. The many conceivable additional reactions involving various electron donor and acceptor pairs are the significant complicating feature since their explicit inclusion seems unavoidable.

It is the purpose of this paper to present a model of sediment oxygen demand which attempts to solve the problem in a fashion which ultimately dispenses with the complexity and relates sediment oxygen demand

to the flux of the oxygen equivalents of all reduced substances in the interstitial water without specific regard to their identity. In fact, since a simple aggregate measure of the oxygen equivalents is available - chemical oxygen demand - a conclusion implicit in the model is that SOD can be determined by measuring the COD flux directly, or by measuring the interstitial water COD profile and measuring or estimating sediment-water mass transfer or diffusion coefficient. Alternately, SOD can be calculated from a mass balance model of oxygen equivalents in the sediment itself. A calculation of the detailed redox chemistry of the sediment interstitial water is also possible and may be required for a detailed understanding of the situation. However, the COD flux methods may suffice in most cases.

The justification for this procedure is based upon two assumptions: (1) that the redox chemistry is at, or reasonably near, thermodynamic equilibrium which leads to the conclusion that COD flux and sediment oxygen demand are identical; (2) that the transport coefficients of the dissolved chemical species involved are independent of their identity which dispenses with the requirement that detailed redox chemistry be computed. If these assumptions are practical approximations, then sediment oxygen demand (the flux of dissolved oxygen from the overlying water to the sediment) is equal to the upward flux of dissolved oxygen equivalents, i.e., dissolved COD, from the sediment. The latter is computed from the decay rate of sedimentary particulate organic COD in the sediment, and the vertical transport mechanisms of diffusion and sedimentation. The demonstration of this fact requires that a model of sediment - interstitial water interactions and transport be formulated and analyzed.

Structure of the Analysis.

The model presented below is based on a number of somewhat different approaches to the analysis of sediment behavior and redox reactions. The first are exemplified by the mass balance models of observed increases or decreases in interstitial water concentrations of substances which are essentially unreactive or, as in the case of radionuclides, have known decay rates (Goldberg and Koide, 1963, Lerman and Taniguchi, 1972). Analogous formulations are available for bacterially mediated reactions which can be assumed to follow simple zero or first order kinetics (Berner, 1974, 1980). These latter are often called diagenetic models and are based on the principle of mass conservation expressed as a mass balance equation. They account for the mass fluxes of diffusion due to molecular and mechanical mixing of the intersititai waters, of advection due to sedimentation and compaction, and the effects of the particulate organic matter decomposition reactions. Typically these models are applied to a single constituent of interest, e.g. ammonia. For multiple constituents a conceptual simplification is available if the reactions are thought of as being driven by the decay of organic matter of a fixed stoichiometry (Richards, 1965). This is also a mass balance approach since equivalents of each electron acceptor are treated similarly and the quantities of substances utilized or produced are in stoichiometric ratios. Both of these approaches utilize the fundamental concept of mass balance expressed either as an algebraic stoichiometric relation or as a mass balance differential equation.

The second principle of importance is that of chemical equilibrium, in particular the observation that interstitial waters are in, or approach, chemical equilibrium. For certain inorganic dissolved species

and certain redox reactions this is a well known approximation that has been tested by a number of investigators (e.g. Garrells and Christ, 1965; Kramer, 1964; Thorstenson, 1970). The evidence comes from evaluating the mass action equations. Mass balance is not usually a factor in these evaluations. While it has often been pointed out that overall and complete thermodynamic equilibrium is never attained for all species in all settings it is also clear that certain reactions occur so quickly that they are virtually in equilibrium over the time scale of sediment mass transport and diagenetic reactions. Thus, while not as universally applicable as the principle of mass balance, it is nonetheless a useful approximation in certain contexts.

The model of sediment behavior presented below is a synthesis of these ideas. The equations of mass balance and chemical equilibrium are combined into a single structure for the analysis of sediment interstitial water concentrations. Since bacterially mediated kinetics are in fact responsible for many of the redox reactions which affect interstitial water concentrations, it might seem at first glance that the principle of chemical equilibrium is of little value in this context. However, it has been pointed out that the thermodynamically predicted sequence of oxidation-reductions is commonly observed in nature as oxidation of organic material occurs (Stumm, 1966) so that this appears to be a reasonable simplification of the complex reaction kinetics actually taking place. The assumption is also quite convenient since equilibrium calculations are independent of the reaction pathways and no detailed specification of the kinetics are necessary. Only the thermodynamic constants of the species of interest are required if detailed species concentrations distributions are to be computed.

If reactions are known not to occur for kinetic reasons even if they are thermodynamically favored, they can be prevented from occurring in the equilibrium calculation as well. Thus, a distinction is made between fast, slow, and prohibited reactions. Fast reactions are those which are assumed to be in (metastable) thermodynamic equilibrium over the time scale of the analysis. Slow reactions are those for which the kinetics are important and must be specified. Prohibited reactions are those which are thought not to occur at all during the time scale of the analysis even if they are thermodynamically favored. The nitrogen system is the most important example for which thermodynamic equilibrium is not useful. If it happens that most reactions are of the fast type then the approach presented below is a major simplification since the number of parameters required to specify the behavior of the species of interest is substantially reduced and a comprehensive analysis is possible.

The major complicating feature of such an analysis is that the chemical species in the interstitial waters that are affected by the fast reactions are also subject to transport via diffusion and other mechanisms. Hence mass transport and rapid reactions are both simultaneously affecting concentrations. As various species are transported the reactions adjust in complex ways to maintain equilibria. The technique presented below for analyzing coupled mass transport with rapid reversible reaction kinetics is based on a transformation of the species mass balance equations into a set of smaller and simpler equations. These equations do not explicitly contain the sources and sinks due to the fast reversible kinetic reactions that cause the analytical and computational difficulties. As a result they can then be solved more directly together with the mass action equations for which there are available computa-

tional codes (e.g., Deland, 1967; Morel and Morgan, 1972.)

Conservation of Mass Equations.

Consider the simplest setting, a one-dimensional vertical analysis of N_s chemical species with names, A_i, at temporal steady state. Let D_i be the diffusion coefficient porosity product of species A_i and let w_i be the corrected (Imboden, 1975) advective velocity of A_i, the velocity induced by the sedimentation of mass relative to a coordinate system fixed with respect to the sediment surface, corrected for compaction, and assume they are constants in depth. Suppose that there exists N_r fast reversible chemical reactions involving the species A_i. The rate at which A_i is produced by reaction j is $\nu_{ji}R_j$, where R_j is the difference between the backward and forward reaction rates of the j^{th} fast reversible reaction and ν_{ji} is the reaction stoichiometry. Let S_i be the net source of A_i due to other reactions which are occurring at slow rates and, therefore, not explicitly included in the fast reversible reaction set. For this situation the conservation of mass equations for the concentration of each species, $[A_i]$, are:

$$- D_i \frac{d^2[A_i]}{dz^2} + w_i \frac{d[A_i]}{dz} = S_i + \sum_{j=1}^{N_r} \nu_{ji} R_j \qquad i=1,\ldots,N_s \qquad (1)$$

The difficulty with solving these coupled nonlinear equations directly is that the forward and backward reaction rates for each fast reaction, R_j, correspond to very short time scales. Further, all that is usually known for these fact reactions is the ratio of the forward to backward reaction rate, i.e., the equilibrium constant. Finally, there are N_s coupled nonlinear equations to be solved simultaneously, which can be a substantial computational burden for a realistic sediment calculation.

It has been suggested (Shapiro, 1962; Galant et al.; 1973) that various transformations be employed to make eqs. (1) more tractable. The crux of the idea is to eliminate the terms $\Sigma_j \nu_{ji} R_j$ which cause the difficulty and replace eqs. (1) with an alternate set of equations. The following fact (Di Toro, 1976) leads to a convenient choice for the transformation: Let B_j, j=1,..., N_c be the names of N_c components and let a_{ij} be the quantity of component B_j in species A_i, i.e. its stoichiometry in terms of the components. The components are the building blocks of the species. For example, the constituent atoms can be used as components. Then, for a set of component conserving reactions the formula matrix with elements a_{ij} is orthogonal to the reaction matrix with elements ν_{ji}, i.e.:

$$\sum_{k=1}^{N^s} \nu_{jk} a_{ki} = 0 \qquad k=1,\ldots,N_c; \qquad j=1,\ldots,N_r \tag{2}$$

The physical fact embodied in these equations is that any reasonable reaction stoichiometry must conserve the component concentrations. This is apparent if the components that make up the species are thought of as the neutral atoms, together with electrons to provide the appropriate charges. All physically realistic (non-nuclear) reactions must conserve atoms and charge, and eq. (2) is just a statement of that fact. It is also apparent that the specific choice of components is not important since any consistent choice is a linear combination of neutral atoms and electrons and, therefore, must also be conserved. This fact suggests that the conservation equations be transformed by multiplying eqs. (1) by the transpose of the formula matrix yielding:

$$\sum_{i=1}^{N^s} \left(-D_i \frac{d^2}{dz^2} + w_i \frac{d}{dz}\right) a_{ik}[A_i] = \sum_{i=1}^{N^s} a_{ik} S_i + \sum_{j=1}^{N^r} R_j \sum_{i=1}^{N^s} a_{ik} \nu_{ji} \tag{3}$$

But the orthogonality relation, eq. (2), implies that the terms involving R_j are zero so that eq. (3) becomes:

$$-\sum_{i=1}^{N_s} a_{ik} D_i \frac{d^2[A_i]}{dz^2} + \sum_{i=1}^{N_s} w_i a_{ik} \frac{d[A_i]}{dz} = \sum_{i=1}^{N_s} a_{ik} S_i \qquad (4)$$

This is the fundamental simplification which makes the analysis tractable. The transformed equations are no longer functions of the fast reversible reactions. They are influenced only by the species mass transport coefficients and the slow reactions, S_i.

It is clear from the derivation of the transformed equations that the simplifications introduced, namely temporal steady state and spatially invariant transport coefficients, do not restrict the applicability of the transformation technique. The method is directly applicable to more general equations which consider temporarily and spatially variable parameters.

Species Independent Transport

If D_i and w_i are not species dependent, the summations $\Sigma_i a_{ik}[A_i]$ in the left-hand side of the above equation become the component concentrations, $[B_k]$, by the definition of a_{ij}. Therefore, the transformation yields conservation of mass equations for the N_c component concentrations:

$$-D \frac{d^2[B_k]}{dz^2} + w \frac{d[B_k]}{dz} = \sum_{i=1}^{N_s} a_{ik} S_i \qquad k=1,\ldots,N_c \qquad (5)$$

These equations are independent of the fast reversible reactions, which can now be assumed to be at equilibrium. Once the spatial distribution of the N_c components, B_k, are calculated from eq. (5) the N_s-N_c equilib-

rium mass action equations for A_i, can be used in conjunction with the N_c stoichiometric algebraic component mass balance equations to solve for the concentrations of the N_s species, $[A_i]$, at any depth of interest, independent of any other depth, a considerably simplified computational task. Thus the components can be treated in exactly the same way as any other variable in simple mass transport calculation, without regard to the reversible reactions, so long as the mass transport coefficients are independent of the species.

For precipitation-dissolution reactions which may be of importance in sediments this simplification amounts to assuming that the solid phase is subject to the same mass transport as the interstitial water, which is clearly not the case. For species-dependent mass transport eqs. (3) must be addressed directly and a method for their numerical solution, which is a good deal less elaborate than what would be required for eqs. (1), is available (Di Toro, 1980).

Sediment Oxygen Demand.

To apply these general principles to the modeling of sediment oxygen demand it is important to realize that the assumption of species independent transport for the fast reactants is all that is required for each component mass balance equation (5) to be independent of the other component equations and the detailed species distribution. Therefore we need only to be concerned with the oxygen consuming component of the sediment chemistry.

Consider the following model formulation. Assume that the principle rate limiting kinetic reaction occurring in sediments is the bacterial conversion or, as it its termed, the diagenesis of particulate sedimen-

tary organic material, $C_aH_bO_cN(s)$, into an available reactive form, $C_aH_bO_cN(aq)$, after which it reacts reversibly and rapidly with all other dissolved species in the interstitial water. In order that species-independent transport is a reasonable assumption the possibility of precipitation or dissolution of solid phase chemical species e.g. $Fe(OH)_2(s)$, is specifically excluded as is the possibility of gas phase formation (bubbles). Thus the model includes the possibility of aqueous phase redox reactions but excludes the possibility of other phase formations and dissolutions which would have different mass transport coefficients. In fact, as shown subsequently, even in the presence of a distinct gas phase, this simplified approach is useful. The modifications required for consideration of solid phase interactions are discussed below. Schematically the reaction sequence is:

$$C_aH_bO_cN(s) \rightarrow C_aH_bO_cN(aq) \rightleftarrows A_1 \rightleftarrows \ldots \rightleftarrows A_{N_s} \tag{6}$$

where $A_1, \ldots, A_{N_s}$ are the rapidly reacting dissolved species being considered. The initial rate limiting reaction controls the rate of the entire reaction set since it is assumed that all other reactions occur rapidly.

The key to a comprehensible result is the intelligent choice of the components which isolates oxygen in oxic conditions. A number of possibilities are:

$$C_aH_bO_cN(s) = a[C] + b[H] + c[O] + [N] \tag{7}$$

the neutral atoms, or the more conventional choice for chemical equilibrium calculations:

$$C_aH_bO_cN(s) = \alpha[CO_2] + \beta[H^+] + \beta[e^-] + \delta[H_2O] + [NH_3] \tag{8}$$

However, the best choice is simply:

$$C_aH_bO_cN(s) = \alpha[CO_2^*] + \beta[O_2^*] + \delta[H_2O] + [NH_3^*] \quad (9)$$

so that particulate organic matter is thought of as being composed of the components: oxidized carbon, CO_2^*, the oxygen required to oxidize the carbon (the COD), O_2^*; and ammonia. That is:

$$C_aH_bO_cN(s) = (CO_2^*)_\alpha(O_2^*)_\beta(NH_3^*) \quad (10)$$

The superscript is used to denote components rather than the species $CO_2(aq)$ and $O_2(aq)$. The production or consumption of H_2O is ignored since it is present in excess. If species independent transport is a reasonable assumption then each component distribution is independent of each other and each component can be considered separately. This is the principle simplification.

Since oxygen consumption is our primary concern, consider the diagenetic decay of particulate COD via a first order reaction for a purely advective sediment model which is the conventional formulation for stationary sediments in lakes and estuaries (Berner, 1980). The mass balance equation for this situation is:

$$w \frac{d[PCOD]}{dz} = -K[PCOD] \quad (11)$$

so that the vertical distribution of particulate COD in the sediment is:

$$[PCOD](z) = \frac{J_{PCOD}}{w} e^{-Kz/w} \quad (12)$$

where J_{PCOD} is the particulate COD flux from the overlying water to the sediment surface. The source of oxygen equivalents to the intersititnl water is $-K[COD](z)$, the negative sign corresponding to the convention that positive COD is oxygen consumed so that positive COD produces negative oxygen equivalents. Thus, the oxygen equivalent component equation is:

$$-D \frac{d^2[O_2^*]}{dz^2} + w \frac{d[O_2^*]}{dz} = \frac{-K}{w} J_{PCOD} e^{-Kz/w} \qquad (13)$$

whose solution is:

$$[O_2^*](z) = [O_2^*]_o - \frac{J_{PCOD}/w}{1 + KD/w^2} (1 - e^{-Kz/w}) \qquad (14)$$

where $[O_2^*]_o$ is the oxygen component concentration at z=o.

The computation of the surface flux of oxygen equivalents follows from its definition $J_{O_2^*} = -D\, d[O_2^*]/dz$ and applying this to eq. (14) yields:

$$J_{O_2^*} = \frac{\eta}{1 + \eta} J_{PCOD} \qquad (15)$$

where $\eta = KD/w^2$. The fraction $\eta/(1+\eta)$ is that portion of J_{PCOD} which is mineralized and returned to the sediment-water interface. The remainder is buried via sedimentation of interstitial water as shown subsequently.

If the particulate COD is composed of various fractions with different diagenetic reaction rates, K_i, then by superposition of solutions:

$$J_{O_2^*} = \sum_i \frac{\eta_i}{1 + \eta_i} J_{PCOD_i} \qquad (16)$$

where $\eta_i = K_i D/w^2$. For example, if a portion of the particulate COD flux is the labile fraction of algal carbon with a relatively rapid reaction rate, then $\eta >> 1$ and all the PCOD flux returns as oxygen equivalents flux. Refractory particulate COD on the other hand may react so slowly that $\eta < 1$ and only a portion is returned. The remainder is buried faster than the reaction can decompose it and diffusion transport it to the sediment-water interface. Table 1 presents examples of the fraction of organic matter that actually reacts diagenetically, the observed

TABLE 1. DECOMPOSABLE FRACTION AND SEDIMENT REACTION RATES

Component	Fraction Reacted	Reaction Rate (yr^{-1})	n	Sediment	Reference
COD	0.13-0.25[a]	0.55-1.9	-	English River Muds	Fair et al., 1941
COD	0.13-0.48[a]	2.4-3.6	-	Sewage Solids and Inert Material	"
Organic N	0.41	0.60[b] 0.013	- 3.9	L.I. Sound (Foam Site)	Berner, 1980
Organic C	0.67	0.0172	52.0	Lake Greifensee	"
Organic N	0.52[c]	0.029	390	Lake Erie Central Basin	Di Toro and Guerriero, in press
Organic C	0.45[c]	0.196	2700	"	

[a] Assuming 0.5 kgC/kg VSS, 2.67 kgO_2/kgC

[b] The larger value in bioturbation zone.

[c] Considering refractory and unreactive fractions only. Labile fraction mineralizes rapidly in the first surface layer.

diagenetic reaction rates and η. The reacted fraction corresponds to the difference between the initial (t=o for batch reaction experiments) or surface (z=o for the analysis of sediment core data) and final ($t \to \infty$, $z >> w/k$) organic matter concentrations. The fact that unreacted sedimentary organic matter is found at depth indicates that only a fraction of PCOD reacts diagenetically. Thus in eq. (15) and subsequently, J_{PCOD} refers to the flux of labile and diagenetically reactive PCOD to the sediment.

The importance of the correction $\eta/(1+\eta)$ can be estimated from the examples listed. For the lake examples the correction is ~ 1. For coastal and pelagic ocean sediments, Toth and Lerman (1977) have observed a correlation between K and w for ammonia: $K/w^2 \sim 0.01$ yr/cm^2. For an ammonia diffusivity in sediments of $\sim 10^{-5}$ cm^2/sec (Li and Gregory, 1974), $\eta \sim 3.2$. Thus for coastal and oceanic sediments the burial correction may be significant.

Figure 1 illustrates the model structure for a single diagenetic reaction rate. Particulate COD decays as it advects downward due to sedimentation. It produces negative dissolved oxygen equivalents in the interstitial water - negative since positive COD is by convention the oxygen consumed. Oxygen equivalents also advect downward but, in addition, they are transported via diffusion. Since the oxygen equivalents concentration decreases with depth the direction of the diffusive flux of O_2^* is downward. This is the reverse of the situation where the concentration of a substance increases with depth in the interstitial water, e.g. ammonia, and its diffusive flux is upward. Hence oxygen equivalents are being transported downward from the water column to the sediment via diffusive exchange.

OXYGEN EQUIVALENTS MODEL OF SOD

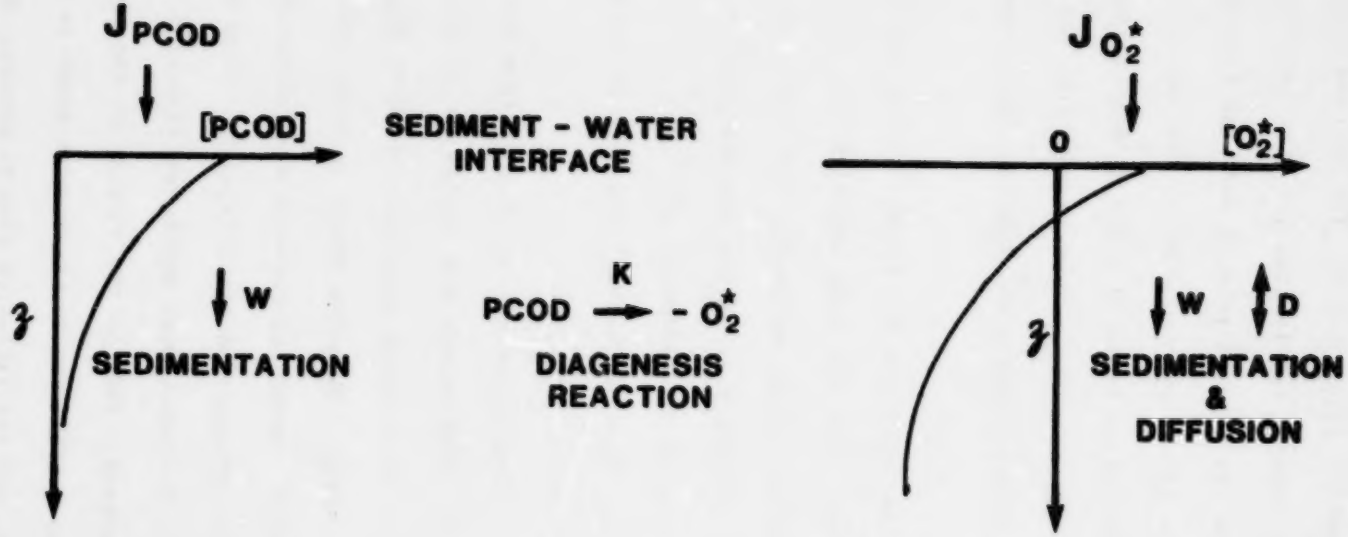


Fig. 1 Schematic representation of the diagenetic oxygen equivalents model of SOD.

It remains only to argue that the flux of oxygen equivalents to the sediment is equal to the sediment oxygen demand itself. Consider the sediment-water interface with aerobic overlying water. At the surface there exists a region, however small, which is aerobic. For the choice of components CO_2^* and O_2^*, the thermodynamic equilibrium for a region where dissolved oxygen exists is that all carbon will exist as inorganic carbon, $CO_2^* = \Sigma CO_2(aq)$, and that all oxygen equivalents are dissolved oxygen itself since no other oxic species of oxygen equivalents exists for the C-H-O system. The reason for the choice of components CO_2^* and O_2^* is that the thermodynamic equilibrium solution for the case that $O_2(aq) > 0$ can be obtained by inspection without any numerical calculations. It is simply that $O_2(aq) = O_2^*$. In general the idea is to choose the components for all the species involved in redox reactions at the oxidation states which are known to be present in oxic conditions. Thus, $SO_4^= = SO_4^*$, $Fe(III)^{3+} = Fe(III)^*$ etc. are chosen as components. Species in the sulfur system would be represented as:

$$SO_4^= = SO_4^* \tag{17}$$

$$HS^- = SO_4^* + 1\ H^+ - 2\ O_2^* \tag{18}$$

the carbon-hydrogen-oxygen system as:

$$O_2(aq) = O_2^* \tag{19}$$

$$CO_2(aq) = CO_2^* \tag{20}$$

$$CH_4(aq) = CO_2^* + 2\ H_2O^* - 2\ O_2^* \tag{21}$$

the iron system as:

$$Fe^{3+} = Fe^*(III) \tag{22}$$

$$Fe^{2+} = Fe(III)^* - H^* + 1/2\ H_2O^* - 1/4\ O_2^* \tag{23}$$

and so on. Note that for this choice of components the only species that contains the component O_2^* that is known to be present in signifi-

cant concentrations in oxic conditions is $O_2(aq)$ itself. Thus the molar concentration of O_2^* must be accounted for by $O_2(aq)$ so that $[O_2^*] = [O_2(aq)]$. It follows that their gradients are equal in oxic conditions, $d[O_2^*]/dz = d[O_2(aq)]/dz$. Therefore SOD, which is the flux of $O_2(aq)$ at the sediment-water interface, z=o, is:

$$SOD = - D \left.\frac{d[O_2(aq)]}{dz}\right|_{z=o} = J_{O_2(aq)} = J_{O_2^*} = \frac{\eta}{1+\eta} J_{PCOD} \qquad (24)$$

Note that the argument that $J_{O_2(aq)} = J_{O_2^*}$ requires that thermodynamic equilibrium is achieved where $O_2(aq) > 0$. This is equivalent to assuming that all reduced compounds are completely oxidized in the aerobic zone at or near the sediment-water interface.

This may not be entirely the case so that a modification of the form:

$$\text{particulate COD} \xrightarrow[K_1]{} \text{soluble COD} \xrightarrow[K_2]{} \text{oxygen equivalents} \qquad (25)$$

where K_1 is the diagenetic reaction rate and K_2 is a faster, but still finite, reaction rate which considers the soluble COD as a slow reactant which can diffuse to the interface and escape as an unoxidized flux of COD as well as being converted to oxygen equivalents. Some evidence that this is the case is suggested by experimental measurements summarized in Table 2. Aerobic dissolved COD fluxes have been measured together with anaerobic COD fluxes and SOD. It is important to note that the difference $J_{O_2^*}(O_2(aq) = 0) - J_{O_2^*}(O_2(aq) > 0)$ equals the measured SOD, confirming the model prediction that the reacted COD flux under aerobic conditions equals the SOD. An empirical correction to account for incomplete reaction is to introduce a fraction, $f_{O_2^*}$, of the anaerobic COD flux which actually reacts aerobically so that:

TABLE 2. COMPARISON OF OBSERVED COD FLUX AND SOD

Anaerobic COD flux (gO_2/m^2-d)	Aerobic COD flux (gO_2/m^2-d)	Difference (gO_2/m^2-d)	Observed SOD (gO_2/m^2-d)	Reference
10.6-11.9	3.7-4.2	6.4-8.2	7.3	Fillos & Molof (1972)
0.408	0.092	0.316	0.292	Lauria & Goodman (1983)

$$SOD = f_{O_2}^* \; J_{O_2}^* \tag{26}$$

From the data in table 2, $f_{O_2}^* \sim 0.65 - 0.80$. Fig. 2 illustrates the model framework with $f_{O_2}^* = 1$ and n large for the sake of clarity.

The upward flux of dissolved COD is equal to the downward flux of oxygen equivalents by the definition of O_2^*. In the aerobic zone the oxidation is complete assuming $f_{O_2}^* = 1$ and thermodynamic equilibrium prevails. All the carbon exists as inorganic carbon and the dissolved oxygen concentration equals O_2^* so that the downward flux of dissolved oxygen is equal to the upward flux of COD.

The specific geometric and transport model used for the sediment is not critical. For example a well mixed sediment layer of depth, H, may be more appropriate. Also the sequence of particulate COD oxidation need not be restricted to a single first order reaction. For example if sedimenting algal and detrital carbon are the sources of particulate COD, then both labile, $PCOD_\ell$, and refractory, $PCOD_r$, components can be considered. The reaction sequence is:

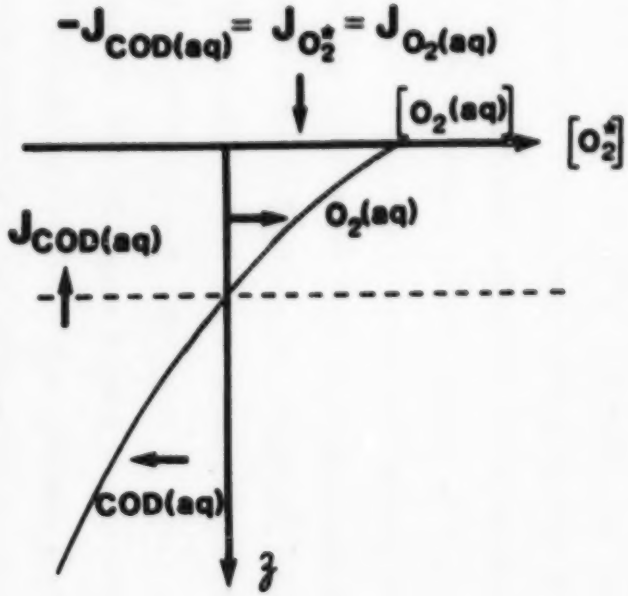
$$\begin{aligned} PCOD_\ell &\xrightarrow{K_\ell} f_r \; PCOD_r - (1 - f_r) \; O_2^* \\ PCOD_r &\xrightarrow{K_r} - O_2^* \end{aligned} \tag{27}$$

where f_r is the refractory PCOD component of the algal carbon. The mass balance equations are analogous to eq. (4) and at steady state the oxygen equivalents flux becomes (Di Toro and Connolly, 1980):

$$J_{O_2}^* = \frac{J_{PCOD_r}}{(1 + \frac{wH}{D'})(1 + \frac{w}{K_r H})} + \frac{J_{PCOD_\ell}}{(1 + \frac{wH}{D'})(1 + \frac{w}{K_\ell H})} (1 - f_r + \frac{f_r}{1 + \frac{w}{K_r H}}) \tag{28}$$

where D' is the effective interstitial diffusion rate for the well mixed layer. In fact for this type of model the parameter D'/H, a mass trans-

FLUXES OF INTERSTITIAL WATER COD, OXYGEN EQUIVALENTS, AND DISSOLVED OXYGEN



AEROBIC LAYER , $O_2^* > 0$

$O_2^* = O_2(aq)$

$CO_2^* = \sum CO_2(aq)$

ANAEROBIC LAYER , $O_2^* < 0$

$O_2^* = -COD(aq)$

$CO_2^* = \sum CO_2(aq) + TOC(aq)$

Fig. 2 Equilibrium thermodynamic distributions of carbon and oxygen components in the aerobic and anaerobic layers.

fer coefficient is the more fundamental parameter group. The dimensionless group wH/D' controls the rate of burial of PCOD relative to the upward diffusion of O_2^*. The residence time decay product of $PCOD_r$ and $PCOD_\ell$ respectively in the active layer are w/K_rH and $w/K_\ell H$. If these groups are all small relative to one then $J_{O_2^*} = J_{PCOD_r} + J_{PCOD_\ell}$ and all the PCOD flux to the sediment returns as SOD. This single layer model in its time variable form has been applied as a component in oxygen balance calculation for Lake Erie (Di Toro and Connolly, 1980) and in the Potomac Estuary (Thomann and Fitzpatrick, 1983).

Relationship of SOD to Sediment Ammonia Flux

A consequence of the diagenetic reaction which liberates negative oxygen equivalents to the interstitial water is that the nitrogeneous component of the organic matter is also released. If it is assumed that (1) the fraction of sediment COD and nitrogen that diagenetically reacts is constant for all sediments, (2) that interstitial water COD and ammonia are transported to the sediment-water interface without reactions and that species-independent transport obtains, (3) that all the COD oxidizes ($f_{O_2^*} = 1$) and no ammonia oxidizes, then one would expect that the ratio of SOD to ammonia flux should be a constant ratio. Fig. 3 presents simultaneous measurements from field observations and laboratory experiments for various sediments. If the Redfield stoichiometry (Redfield et al., 1963) was representative of the reactive portion of organic matter then the ratio should be 15 gO_2/gN. The data indicate a range of from 15-30 gO_2/gN for most data and a suggestion that at higher SOD fluxes (> $2gO_2/m^2$-d) only a fraction ($f_{O_2^*} \sim 1/2$) of the COD flux is actually oxidized. The higher ratio suggests that a portion of the ammonia flux to

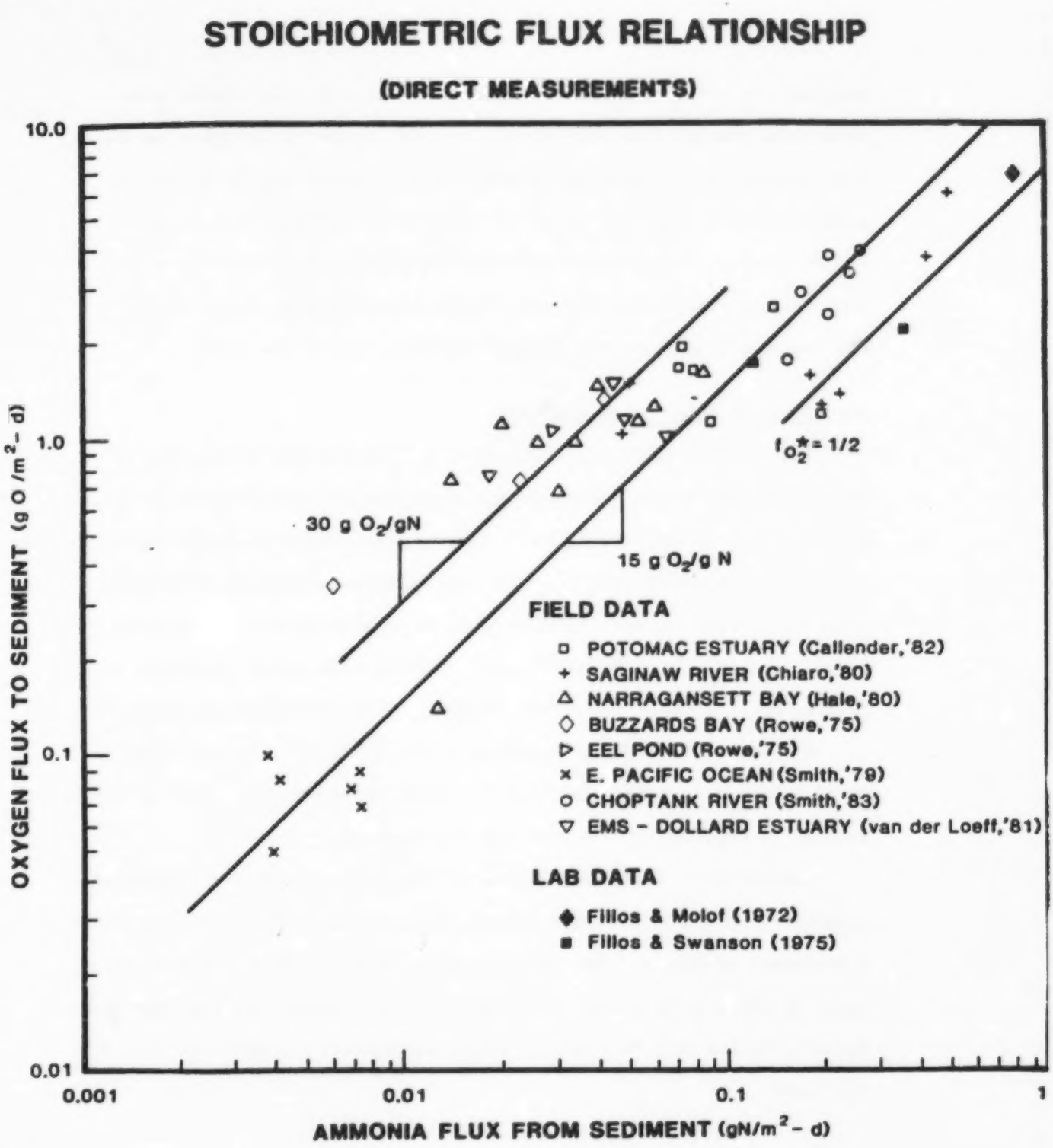


Fig. 3 Observed relationship between SOD and ammonia flux from sediments. Data are from paired observations.

the sediment water interface is oxidized to nitrate. This would both reduce the ammonia flux and increase the SOD, producing a higher ratio. This possibility is discussed subsequently. Considering the variation of observed COD/C and C/N ratios of particulate sediment organic matter and the lack of interstitial water COD/NH_4-N data which would be necessary to more rigorously test this simple stoichiometric relationship, the comparison supports the diagenetic oxygen equivalents model.

The Effect of Solid Phase Reactions

The validity of the eq. (26) which relates the SOD to the flux of particulate COD to the sediment-water interface depends directly on the applicability of the assumption of species independent transport since it is this assumption that decouples the component equations from each other and allows the mass balance of O_2^* to be independent of the other components: CO_2^*, SO_4^*, $Fe(III)^*$, etc. Species independent transport is approximately true for dissolved species - ionic diffusion coefficients in sediments differ by approximately a factor of two (Li and Gregory, 1974) - but it is surely not true for solid phase species. Thus a correction is required for the mass balance equations.

Instead of a detailed analysis of the species-dependent transport equations, consider the mass balance that results from the situation illustrated in fig. 4. The flux of organic PCOD to the sediment is balanced by the flux of oxygen equivalents to the sediment and the loss via burial. To see this in terms of oxygen equivalents consider eq. (15) in the form:

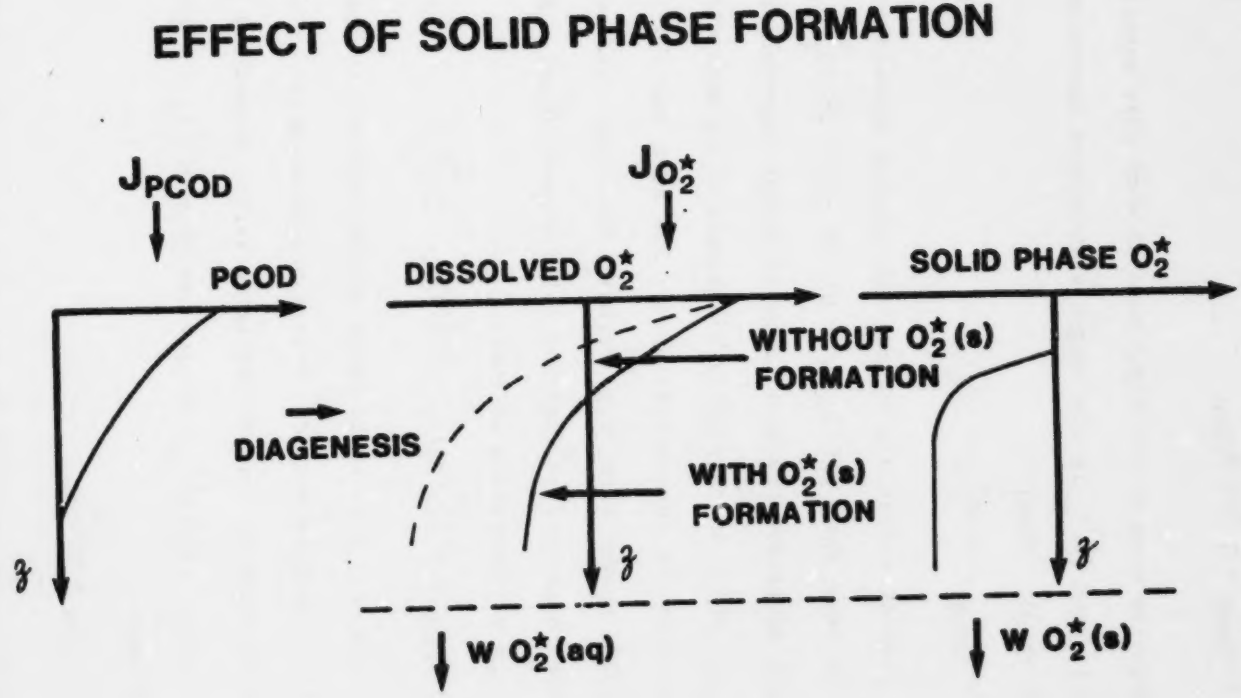


Fig. 4 Mass balance analysis of reduced solid phase formation.

$$J_{O_2}^* = J_{PCOD} - \frac{1}{1+n} J_{PCOD} \tag{29}$$

From eq. (14) the negative term on the right hand side of this equation is: $w\{[O_2^*] - [O_2^*]_\infty\}$ where $[O_2^*]_\infty$ is the oxygen equivalents concentration at large depth ($Kz/w >> 3$). Thus:

$$J_{O_2}^* = J_{PCOD} + w\{[O_2^*]_\infty - [O_2^*]_o\} \tag{30}$$

Note that eq. (14) indicates that the oxygen equivalents concentration $[O_2^*]_\infty$ would either be less than (if $J_{PCOD} > 0$) or equal to $[O_2^*]_o$ (if $J_{PCOD} = 0$) so that the advective transport term is always negative or zero (i.e. $J_{O_2}^* < J_{PCOD}$) which is physically reasonable since some dissolved COD is buried with the interstitial water and does not exert an SOD. When reduced solid phases form, e.g. $Fe(OH)_2$, FeS, etc., the oxygen equivalents are in both dissolved, $O_2^*(aq)$ and solid phases, $O_2^*(s)$. Both of these are buried via sedimentation so that:

$$J_{O_2}^* = J_{PCOD} + w\{[O_2^*(aq)]_\infty + [O_2^*(s)]_\infty - [O_2^*]_o\} \tag{31}$$

The additional flux, $w[O_2^*(s)]_\infty$, of solid phase oxygen equivalents reduces $J_{O_2}^*$ since $[O_2^*(s)]_\infty$ is a negative number. From a practical point of view, the term $w[O_2^*]_o$, the entrainment flux of overlying water, is usually negligible: e.g. $w < 10$ cm/yr, $[O_2(aq)]_o < 10$ g/m^3 so that $w[O_2^*]_o < 1$ g/m^2--yr, and eq. (31) becomes

$$J_{O_2}^* \simeq J_{PCOD} + w[O_2^*]_\infty \tag{32}$$

where $[O_2^*]_\infty$ is the bulk oxygen equivalents concentration of the sediment (aqueous and inorganic solid phase). Thus the proper correction is to

decrement (add a negative number to) $J_{O_2}^*$ to account for the loss due to burial of the reduced solid phases which form. Based upon the relationship observed between ammonia flux and SOD (fig. 3) this correction is probably not significant. A calculation for Lake Erie, presented subsequently, also supports this conclusion. With the exception of this correction the formation of various reduced solid phases has no other effect on the steady state oxygen-equivalents flux and, therefore, the SOD since ultimately the only source of oxygen equivalents is via the sediment-water interface.

The Effect of Ammonia Production

The production of elevated interstitial water concentrations of ammonia is perhaps the most commonly observed consequence of the diagenesis reaction. The examples which follow illustrate the phenomena as does the relationship between ammonia flux and SOD (fig. 3). It is conventional to assume that ammonia is conservative in the anaerobic zone and computations based on this assumption are representative of the observations (Berner, 1980).

With regard to sediment oxygen demand, it is possible that ammonia in the aerobic zone can nitrify to a significant extent and consume oxygen as a consequence. However if the aerobic layer is thin and the overlying water DO is depressed then nitrification is unlikely since nitrifying bacteria require $\sim$ 1-2 mg O_2/ℓ for nitrification.

If nitrification is occurring in the sediment then it is also possible that a portion of the nitrate produced diffuses into the anaerobic region where it is denitrified. The overall reaction in that case would be

$$\frac{1}{3} NH_3 + \frac{1}{4} O_2^* \rightarrow \frac{1}{6} N_2 + \frac{1}{2} H_2O \qquad (33)$$

so that the stoichiometric consumption ratio is 1.7 $gO_2/g\ NH_3$-N instead of 4.57 gO_2/gNH_3-N for nitrification. Typical carbon/nitrogen ratios of sediments $\sim$ 10 so that even for no denitrification the ratio of carbon to nitrogen assiciated SOD would be $\sim$ (10)(2.67)/(4.57)(1) = 5.8 that is $\sim$ 86% of the total SOD is derived from carbon associated diagenesis. With denitrification considered the percentage is higher. Hence it is possible that $\sim$ 10-30% additional SOD could be generated by the ammonia and nitrification. However for most cases the thin aerobic layer and low DO concentrations preclude the reaction and ammonia escapes to the overlying water without exerting an SOD.

The Effect of Nitrate flux to the Sediment

Nitrate in the overlying water is subject to the same diffusive flux as is O_2(aq) so that denitrification in the sediment clearly occurs. Unlike the other electron acceptors considered above, however, its function is different. Nitrate reduction is not a reversible process and, therefore, cannot be included in the fast reaction set. It must be considered explicitly. However the rate of denitrification is most probably rapid relative to the diagenesis rates so that an explicit slow reactant approach with its attendant reaction rate is not necessary. Rather it is assumed that all nitrate delivered to the anaerobic zone is rapidly reduced. Since the nitrogen gas produced at this location is a non-reversible endproduct, its formation is a permanent sink of dissolved COD and, therefore, a constant source of oxygen equivalents.

As a simple approximation, assume that the depth of denitrification, L, is at $O_2^* = 0$ the aerobic-anaerobic transition depth. At this depth nitrate is rapidly consumed so that $[NO_3^-](L) = 0$. The situation is illustrated in fig. 5. The flux of nitrate to the sedimentwater interface is:

$$J_{NO_3} = - D \frac{d[NO_3]}{dz} \simeq \frac{D[NO_3]_o}{L} \tag{34}$$

where $[NO_3^-]_o$ is the overlying water nitrate concentration. The oxygen equivalents mass balance equation now has an additional term due to the source of oxygen equivalents provided by denitrification:

$$NO_3^- + \frac{1}{2} N_2 - H^+ + \frac{1}{2} H_2O + \frac{5}{4} O_2^* \tag{35}$$

Thus:

$$- D \frac{d^2[O_2^*]}{dz^2} + w \frac{d[O_2^*]}{dz} = - \frac{K}{w} J_{PCOD} e^{-Kz/w} + J'_{NO_3} \delta(z - L) \tag{36}$$

where $J'_{NO_3} \delta(z - L)$ is the delta function source of oxygen equivalents at location L; $J'_{NO_3} = \frac{5}{4} J_{NO_3}$, and J_{NO_3} is given by eq. (34). The use of the delta function assumes that the depth over which denitrification occurs is small and is representable by a point source of O_2^* at $z = L$. The solution of this equation yields:

$$[O_2^*](z) = [O_2^*]_o - \frac{J_{POD}/w}{1 + KD/w^2} (1 - e^{-Kz/w}) + \frac{J'_{NO_3}}{w} (1 - e^{-wz/D}) \tag{37}$$

for $z < L$. The flux expression follows from its definition:

$$J_{O_2^*} = J_{PCOD} \frac{\eta}{1 + \eta} - J'_{NO_3} \tag{38}$$

In order to evaluate $J'_{NO_3} = D[NO_3^-]_o/L$ the depth of zero nitrate concentration, L, is required. From the condition that $O_2^* = 0$ at $z = L$, eq.

EFFECT OF DENTRIFICATION

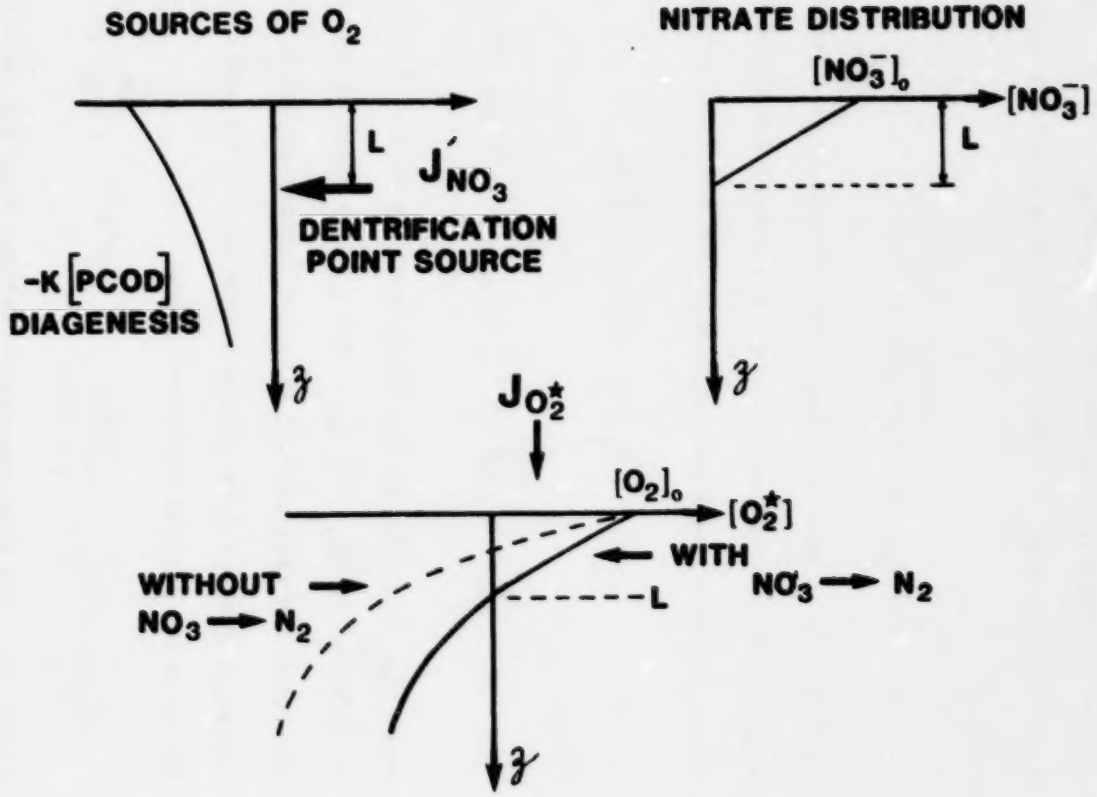


Fig. 5 Framework for the analysis of the effect of overlying nitrate reduction on SOD.

(37) yields:

$$L = \frac{1 + \eta}{\eta} \frac{D([O_2^*]_o + \frac{5}{4}[NO_3^-]^o)}{J_{PCOD}} \quad (39)$$

for the case that KL/w and wL/D << 1, corresponding to a small aerobic depth. Using this expression in eq. (34) and eq. (38) yields:

$$J_{O_2}^* = J_{PCOD} \frac{\eta}{1 + \eta} \left(\frac{[O_2^*]_o}{[O_2^*]_o + \frac{5}{4}[NO_3^-]_o}\right) \quad (40)$$

Thus the presence of nitrate as an irreversible source of oxygen equivalents reduces the flux of O_2^* to the sediment by the ratio: $[O_2(aq)]_o / ([O_2(aq)]_o + \frac{5}{4}[NO_3^-]_o)$. For example if $O_2(aq)$ = 1 mg/ℓ and NO_3-N = 0.1 mg/ℓ then the ratio is: 0.78.

It is disturbing to note that two sets of experiments designed to test this effect (Edwards and Rolley, 1965; Andersen, 1978) both found no significant reduction of SOD as overlying water nitrate concentration increased (0-20 mgN/ℓ) although increased nitrate flux to the sediment was observed. These results are most puzzling. It may be that the steady state assumptions used to obtain eq. (40) did not apply to the experimental observation which may reflect transient conditions. Alternately the presence of increased nitrate flux to the sediment may increase the rate at which diagenesis occurs so that temporarily at least a greater supply of dissolved COD is available that just balances the increase in available oxygen equivalents from the nitrate flux. Again this would reflect a transient phenomena. In any case experimental investigations are required which are designed to evaluate the full oxygen equivalents mass balance before eq. (40) is regarded as more than a speculation. However the underlying fact that a nitrate flux to the sed-

iment coupled with an N_2 flux from the sediment is a net source of O_2^* (i.e. a net sink of dissolved COD) seems inescapable. Thus either more dissolved COD is produced in the presence of nitrate, or eventually the SOD decreases, since the mass balance of oxygen equivalents must apply at steady state.

It is interesting to note that the oxygen equivalents viewpoint predicts that the presence of sulfate in the overlying water has no direct effect, with the exception of the possibility of formation of solid phase reduced sulfur compounds that are lost by burial. The reason is that sulfate reduction produces HS^-, $S^=$, etc. which are reversibly oxidizable. Hence their formation do not provide sinks of dissolved COD which escape oxidation in the aerobic zone as does N_2. Rather, they function as reversible intermediates that transport dissolved COD upward and oxygen equivalents downward. Hence their absolute concentration is unimportant. If they are present in only small amounts, other species are available to perform the same function. This fact explains the observation that SOD's in fresh and salt water are of the same order of magnitude (e.g. fig. 3) whereas the overlying water sulfate concentrations differ by multiple orders of magnitude.

Application to Chesapeake Bay Sediments

The purpose of this example is to illustrate the utility of the formulation that assumes species-independent transport and redox equilibrium for analyzing sediment chemistry and to relate the results to SOD. The data, from Chesapeake Bay sediments (Troup, 1974; Reeburgh, 1967), have been averaged in order to obtain a representative set of observations which are broadly characteristic of the anaerobic sediments of upper

Chesapeake Bay. The solution of eq. (4) for each component, B_k, is as before:

$$[B_k](z) = [B_k]_o + \frac{a_k c_o}{1+KD/w^2}(1 - e^{-Kz/w}) \quad k=1,\ldots,N_c \qquad (41)$$

where $[B_k]_o$ are the component boundary concentration at z=o, the sediment-water interface and a_k is the stoichiometric coefficients of component k in $C_aH_bO_cN(s)$, whose concentration is c_o at z=0. For components that are not part of the stoichiometry of the sedimentary organic matter, their concentrations are constant in depth.

In order to apply this analysis to a specific setting it is necessary to have estimates of the stoichiometry of sedimentary organic matter, a_k, the rate of exponential decrease of the organic matter, K/w, and the leading constant, $c_o/(1+KD/w^2)$ as required by eq. (41). For the calculations presented below the latter two parameter groups are estimated from the observed ammonia profile. Ammonia is assumed to be conservative in the anaerobic portion of the sediment and therefore provides a useful tracer for this purpose. The concentrations of the remaining chemical components are established from observations at the sediment-water interface.

The carbon and oxygen equivalents stoichiometry of the sedimentary organic material can best be obtained from direct measurements. For this illustration an estimate is chosen in order to reproduce the observed profiles of sulfate and total inorganic carbon. Table 3 lists the components considered, the boundary concentrations at the sediment surface, and the estimated stoichiometry. Fig. 6 illustrates the calculated depth distribution of the components used in the calculation. The choice of components is arbitrary with the exception of the electron,

Table 3

Components and Parameter Values for Chesapeake Bay Sediment Analysis

Component	Boundary Concentration	Organic Matter Stoichiometry[a]
B_k	$[B_k]_o$ (mM)	a_k
CO_2	1.001	16.0
H_2O	1060.1	0.0
NH_4^+	1.0	1.0
Ar	0.01325	0.0
H_2S	15.0	0.0
H^+	pH=7.4[b]	50.0
e^-	-123.0	51.0
NH_4^*[c]	0.0625	1.0

(a) Corresponds to $C_{16}H_{50}O_{32}N$

(b) Held constant in the calculation consistent with observation

(c) The slow reactant NH_4^+

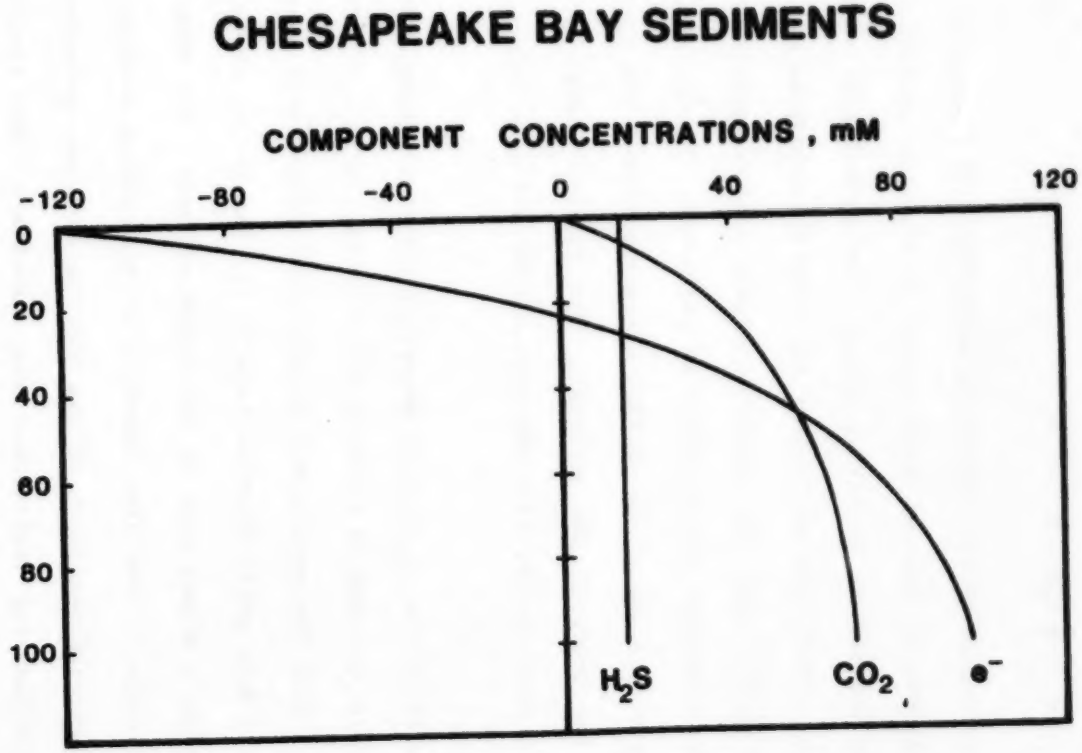


Fig. 6 Computed depth distribution of component concentrations.

which simplifies the chemical equilibrium calculations. With regard to SOD, it can be seen that there must be a flux of electrons to the sediment-water interface where they react with the terminal e-acceptor, $O_2(aq)$ to produce SOD. This is just an alternate viewpoint since electrons and oxygen equivalents are related via:

$$e^- = \frac{1}{2} H_2O - H^+ - \frac{1}{4} O_2^*$$

With the distribution of the components established it remains to compute the concentrations of species which result at chemical equilibrium for the reactions assumed to be taking place. The calculation is conventional (DeLand, 1967); the two phases and species considered are listed in Table 4 together with the appropriate mass action equilibrium constants for the component stoichiometry as indicated. The gas phase forms spontaneously if the sum of the partial pressures exceeds the hydrostatic pressure at the depth of the sediment. The partial pressures of the gases in this phase follow from the mass action and mass balance equations.

The results of the computation described above are shown in fig. 7. The ammonia data are used to estimate $w/K = 30$ cm. and $a_k c_o/(1+KD/w^2) = 4.6$ mM - NH_3. Both the ammonia and sulfate data reflect what appears to be a relatively more rapid reaction rate in the top 10 cm. of the sediment, followed by a slower rate in the deeper sediment. For this illustration the parameters have been chosen as an approximate average of the rates. The observed magnitude of the sulfate decrease determines the electron stoichiometric coefficient and, therefore, the electron to nitrogen ratio of the sedimentary organic material. The carbon to nitrogen ratio is determined by fitting the observed total inorganic carbon increase as shown in fig. 7c.

CHESAPEAKE BAY SEDIMENTS

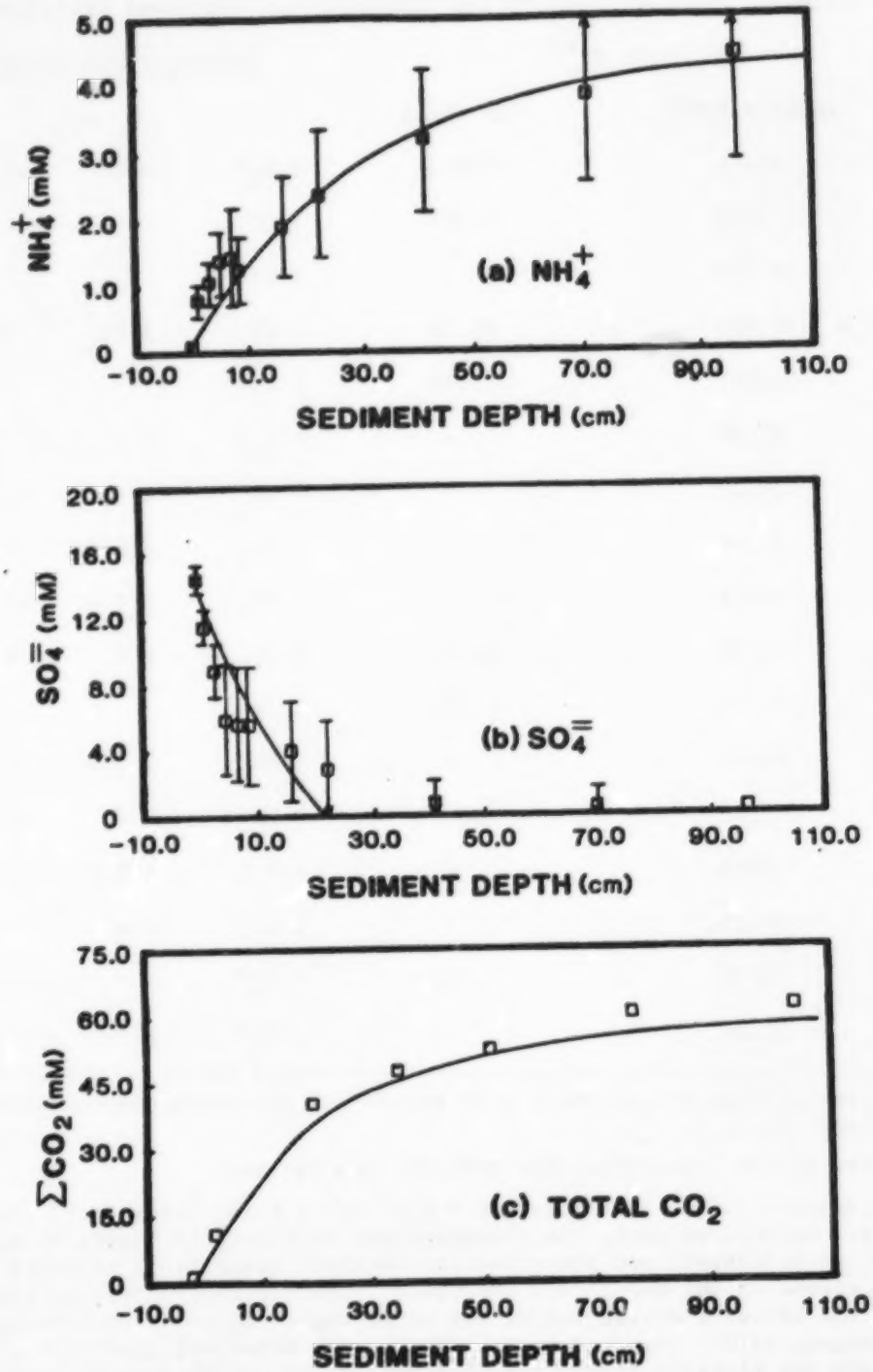


Fig. 7 Observed and computed interstitial water concentrations of ammonia, sulfate, and total carbon dioxide profiles for K/w = 30 cm., $c_o/(1+KD/w^2)$ = 4.6 mM and $C_{16}H_{50}O_{32}N$ stoichiometry.

Table 4. Species, Equilibrium Constants and Component Stoichiometry

Species	$-\ln K^{(a)}$		Component Stoichiometry			
	AQUEOUS PHASE	GAS PHASE	a_{ij}			
O_2	204.9	198.0	2 H_2O	-4 E-	-4 H^+	
CO_2	3.17	1.386	1 CO_2			
H^+	-0.378	-	1 H+			
$NH_4^+(NH_3)$	-0.430	26.23	1 NH_4^+	1 NH_4^* (b)	(-1 H+)	
H_2O	-0.0053	3.59	1 H_2O			
OH^-	32.95	-	1 H_2O	-1 H+		
HCO_3^-	18.19	-	1 CO_2	1 H_2O	-1 H+	
$CO_3^=$	41.66	-	1 CO_2	1 H_2O	-2 H+	
NO_3^-	283.6	-	1 NH_4^+	3 H_2O	-8 E-	-10 H+
CH_4	-49.68	-54.59	1 CO_2	8 H+	8 E-	-2 H_2O
Ar	6.515	1.386	1 Ar			
NO_2^-	216.9	-	1 NH_4^+	2 H_2O	-8 H+	-6 E-
N_2	122.2	116.2	2 NH_4^+	-8 H+	-6 E-	
$SO_4^=$	98.8	-	1 H_2S	4 H_2O	-10 H+	-8 E-
HS^-	18.88	-	1 H_2S	-1 H+		
H_2S	2.58	0.0	1 H_2S			
$S^=$	50.84	-	1 H_2S	-2 H+		

(a) For aqueous phase concentrations in mole/ℓ and gas phase concentrations in mole fractions.

(b) Included in the calculation for ammonia conservative.

(c) Temperature = 15°C, Ionic Strength = 0.39 and a total pressure of four atmospheres. Calculated using the thermodynamic constants of Wagman et al (1968) except as indicated, and corrected for sediment temperature assuming the tabulated values of ΔH_f° and S° are constants. Ionic strength corrections are made using the Davies modification of the Debye-Huckel activity coefficients (Stumm and Morgan, 1970). Aqueous solubility for the dissolved gases are obtained from Atkinson and Richards (1967) and Yamamoto et al (1976) and CH_4, Harvey (1966) for CO_2, and Weiss (1970) for N_2 and Ar, corrected for the observed chloride concentration and temperature.

With the stoichiometry fixed, the methane concentration and the behavior of the gas phase are determined by the equilibrium assumption and the solubilities of the dissolved gases. The calculated and observed dissolved methane, nitrogen and argon are shown in fig. 8. These data provide independent support for the calculation since the free parameters have been estimated using the other data.

A number of features are noteworthy. The calculation correctly reproduces the observed rapid increase of methane commencing at a depth of 20 cm and reaching a plateau concentration of approximately 6mM at 50 cm after which the increase is very gradual. The dissolved nitrogen and argon concentrations are calculated to remain constant, consistent with the inert nature of argon and the absence of denitrification, until a depth of approximately 40 cm, after which both concentrations decrease. The nearly constant methane concentration and the decline in dissolved nitrogen and argon results from the equilibrium between the interstitial water concentrations and a gas phase which forms. As the partial pressure of methane increases with depth due to the increasing quantity of dissolved COD which has reacted, the sum of the partial pressures also increases until it equals the total fluid pressure, at which point a gas phase forms. This is calculated to occur at approximately 35 cm. As depth increases more methane is formed, and, since the interstitial waters are saturated with methane, the additional production causes the gas phase to expand. The larger gas phase volume provides a greater dilution volume for the nitrogen and argon gas. Thus the partial pressures of both nitrogen and argon in the gas phase decrease and, consequently, since the interstitial waters are assumed to be in equilibrium

CHESAPEAKE BAY SEDIMENTS

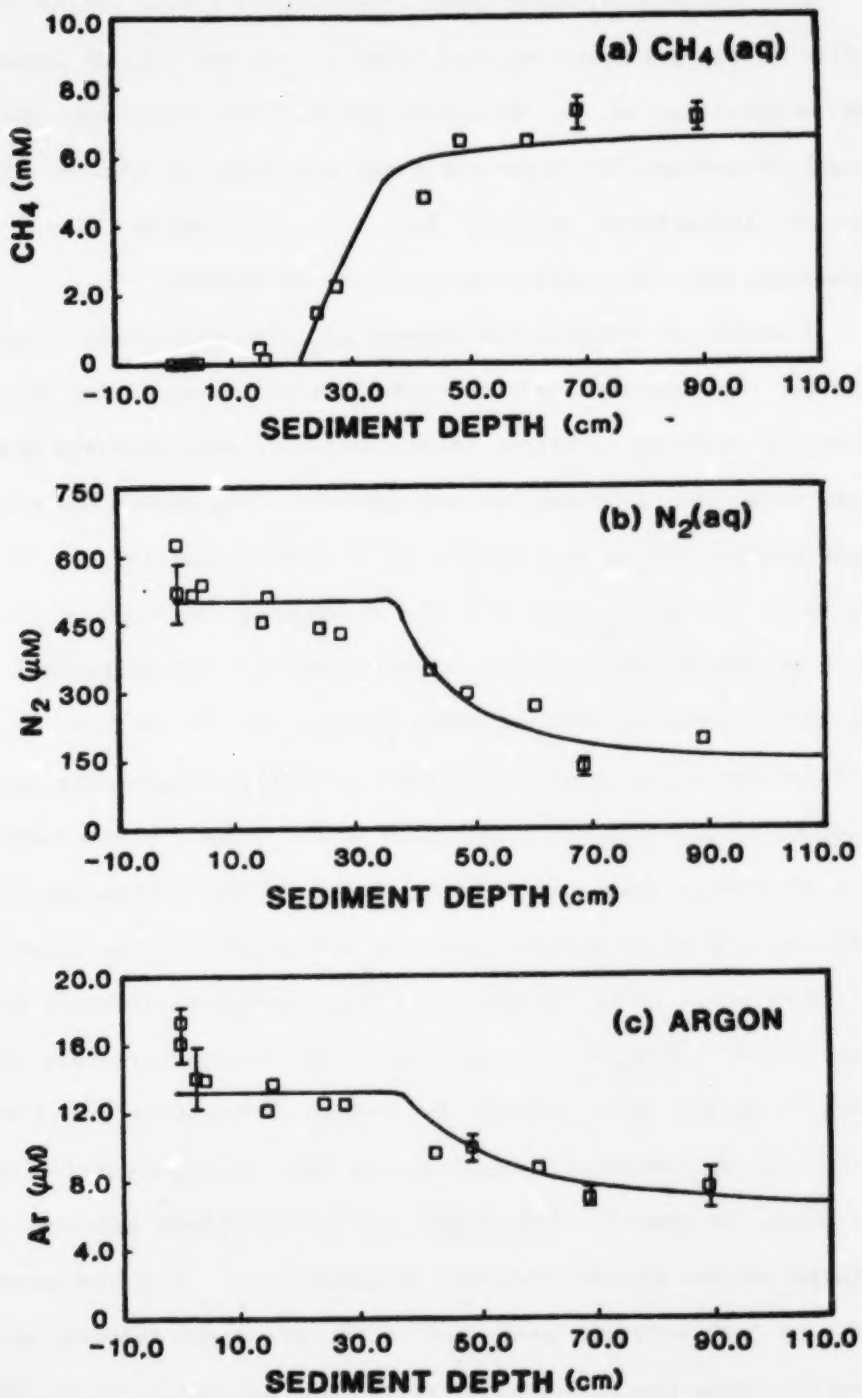


Fig. 8 Observed and computed interstitial water concentrations of dissolved methane, nitrogen, and argon.

with the partial pressures in the gas phase, their concentrations also decrease.

However, the actual quantity of the decrease is different for N_2 and Ar due to their differing solubilities. The calculated and observed N_2/Ar ratio, shown in fig. 9a, illustrates this behavior which, as pointed out by Reeburgh (1969, 1974), is evidence in support of the existence of gas bubbles.

The behavior of the ratio of total aqueous CO_2 to ammonia, fig. 9b, is similar although the underlying mechanism is different. To a depth of 20 cm the ratio is constant at the stoichiometric ratio of the sedimentary organic matter. As methane starts to form the proportions of $\Sigma CO_2(aq)$ and $CH_4(aq)$ produced is a result of the stoichiometry of the organic material and this agreement with observation is further evidence that the calculation is a consistent interpretation of the observed concentrations.

The lack of dissolved methane in the zone of sulfate reduction is a direct consequence of the assumption that the fast reactions involving these species are reversible and approximate thermodynamic equilibria. In kinetic terms this is equivalent to assuming that there exists a set of reactions which allows the oxidation of methane with sulfate as the terminal electron acceptor. As has been pointed out (Barnes and Goldberg, 1976; Reeburgh, 1976; Martens and Berner, 1977), this is the only plausible explanation for these and similar observed profiles in the presence of mass transport. That this reaction is rapid relative to the slow sedimentary organic matter decay is an approximation that appears to be reasonable. If the kinetics of this reaction were slower the result would be methane diffusing into the zone of sulfate reduction.

CHESAPEAKE BAY SEDIMENTS

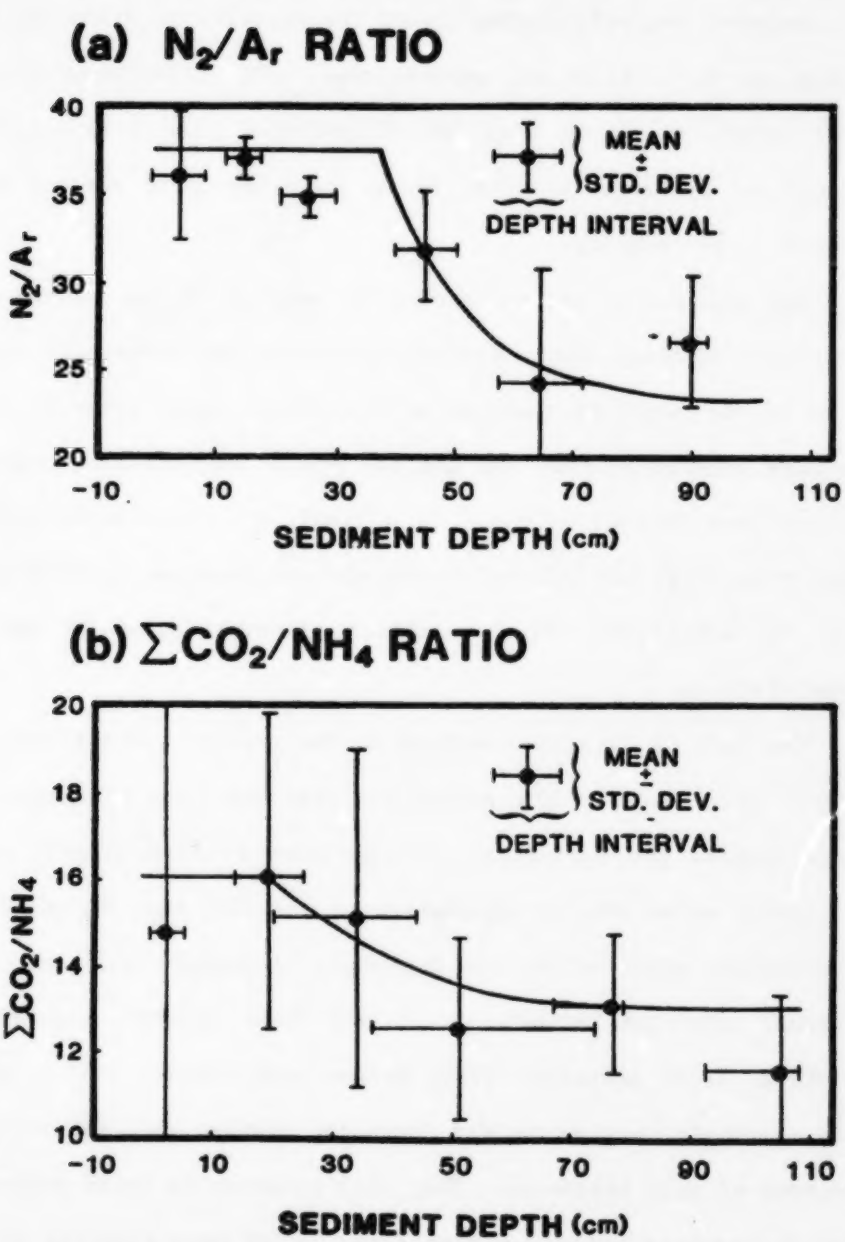


Fig. 9 Computed and observed ratios of (a) Dissolved Nitrogen and Argon (b) Dissolved total Carbon Dioxide and Ammonia. The depth interval corresponds to the ammonia data, since one CO_2 measurement is available for each observation, at the indicated depth.

Although no interstitial water COD data are available, it is straightforward to compute the SOD to be expected from this sediment. Each component's vertical distribution is given by eq. (41) with the appropriate leading stoichiometric coefficient. The differing surface boundary conditions $[B_k]_o$ do not affect the gradient and therefore the flux. Thus:

$$J_{O_2^*} = -\frac{1[O_2^*]}{4[e^-]}\,\frac{123[e^-]}{1[NH_4^+]}\,J_{NH_3} \qquad (42)$$

where:

$$J_{NH_3} = \frac{KD}{w}\,\frac{c_o}{1 + KD/w^2} \qquad (43)$$

For $D \sim 1.0$ cm^2/d the result is an SOD of ~ 1.5 gO_2/m^2-day, an entirely reasonable estuarine value.

The purpose of the preceding example is to illustrate the results that can be obtained using a simple species-independent transport model of sediment redox reactions. A more detailed analysis of these data is available (Di Toro, 1980) which considers independent gas phase transport. The important point is that the reaction sequence is reasonably reproduced with a minimum of effort and that the computed SOD is within the expected range of observation. Another application for which the calculation of sediment oxygen demand is the primary focus is presented below.

Application to Lake Erie

The original application of oxygen equivalents for the modeling of sediment oxygen demand was to Lake Erie, particularly the Central Basin

(Di Toro and Connolly, 1980). The concern was the hypolimnetic depletion of dissolved oxygen due to algal respiration and sediment decomposition. The original formulation was restricted to a 5 cm well-mixed active layer. The computation reproduced the observed SOD, only if an additional flux of oxygen equivalents from the deeper sediment was included. For the calculation presented below, the hypolimnetic water column and the entire active sediment column is jointly considered. The model is one dimensional vertically and at steady state in the sediment. The water column calculations reflect the average conditions for t = 50 days from the onset of stratification.

The nitrogen system transformations are implemented as slow kinetic reactions with sequential first order reactions representing the reaction pathway: Org-N $\rightarrow$ NH_3 $\rightarrow$ NO_3 $\rightarrow$ N_2. Ammonia decay is allowed only in the water column and denitrification occurs only in the sediment. The carbon and oxygen equivalents calculation are implemented using slow kinetics for the diagenesis of the refractory portion and the faster mineralization reaction of the labile and dissolved portion. The end products are the components CO_2^* and O_2^* which react to produce the species concentrations as in the Chesapeake Bay example. No gas phase forms in this example. The reaction rates and boundary conditions imposed at the thermocline are listed in Table 5.

The calibration procedures and the sources of data are described elsewhere (Di Toro and Guerriero, in press). The purpose of this presentation is to illustrate the results of the use of the oxygen equivalents method. Fig. 10 presents the nitrogen cycle and fig. 11 presents the carbon and oxygen results. Each plot illustrates the hypolimnetic concen trations (top half) and sediment concentrations (bottom half) either

TABLE 5

Lake Erie Nitrogen and Carbon Reaction Rates and Boundary Conditions

	Nitrogen		Carbon	
	Reaction Rate (/day)	Boundary Condition mg N/ℓ	Reaction Rate	Boundary Condition mg C/ℓ
Particulate Unreactive	0.0	0.0093	0.0	0.0925
Particulate Refractory	0.029 (/yr)	0.003	0.196 (/yr)	0.006
Particulate Labile	0.01	0.014	0.03	0.052
Dissolved Organic	0.03	0.14	0.03	0.01
Ammonia	0.07[(a)]	0.038	-	-
Nitrate	2.0[(b)]	0.016	-	-
Nitrogen Gas	0.0	9.5	-	-
Chlorophyll[(d)]	0.075	0.035[(c)]	0.075	0.35[(c)]

(a) Water column only, Sediment reaction rate = 0

(b) Sediment only, Water column reaction rate = 0

(c) Corresponds to 3.5 µg Ch/ℓ carbon/chlorophyll = 100; nitrogen/chlorophyll = 10

(d) The stoichiometric pathway of chlorophyll decay is 20% refractory C and N; 20% labile C and N, 10% DOC and DON, and 50% CO_2^*, O_2^*, and NH_3.

as mg/kg of water or dry sediment for particulates, or mg/ℓ of interstitial water for dissolved species. When a discontinuity appears in the computed curve it is due to a plotting scale change at the sediment-water interface. Concentrations are continuous across the sediment-water interface. Particulate slow reactants are settling and dispersing in the water column and only sedimentating in the sediment. Dissolved slow reactants and fast reactant components are dispersing in both the water column and the interstitial water. The diagenetic reaction of particulate refractory organic matter and the more rapid mineralization of particulate labile and dissolved organic matter produce NH_3, CO_2^* and O_2^*. Ammonia builds up in the interstitial water and diffuses to the overlying hypolimnion where it nitrifies to nitrate. NO_3^- in turn diffuses into the sediment where it denitrifies to N_2, and acts as a source of O_2^*. The dissolved N_2 concentration is calculated and, as shown in fig. 10, is less than observations, indicating that either more denitrification is occurring or that it is occurring deeper in the sediment and N_2 more is retained as a result.

The carbon-oxygen computations, fig. 11, follow the same pattern. The slight difference between observed and computed PCOD is due to the assumed COD/Org C ratio of 2.67. The diagenetic reaction is responsible for the gradients of POC and PCOD. The labile particulates mineralize rapidly and are recycled in the first surface layer. Interstitial water COD brackets the few available observations. ΣCO_2 and CH_4 interstitial water distributions are reasonably reproduced as is the dissolved oxygen and sulfate distribution. The computed SOD = 230 mg/m^2-d is slightly lower than the observed range: 280 - 350 mgO_2/m^2-d (see the summary in Adams et al., 1982).

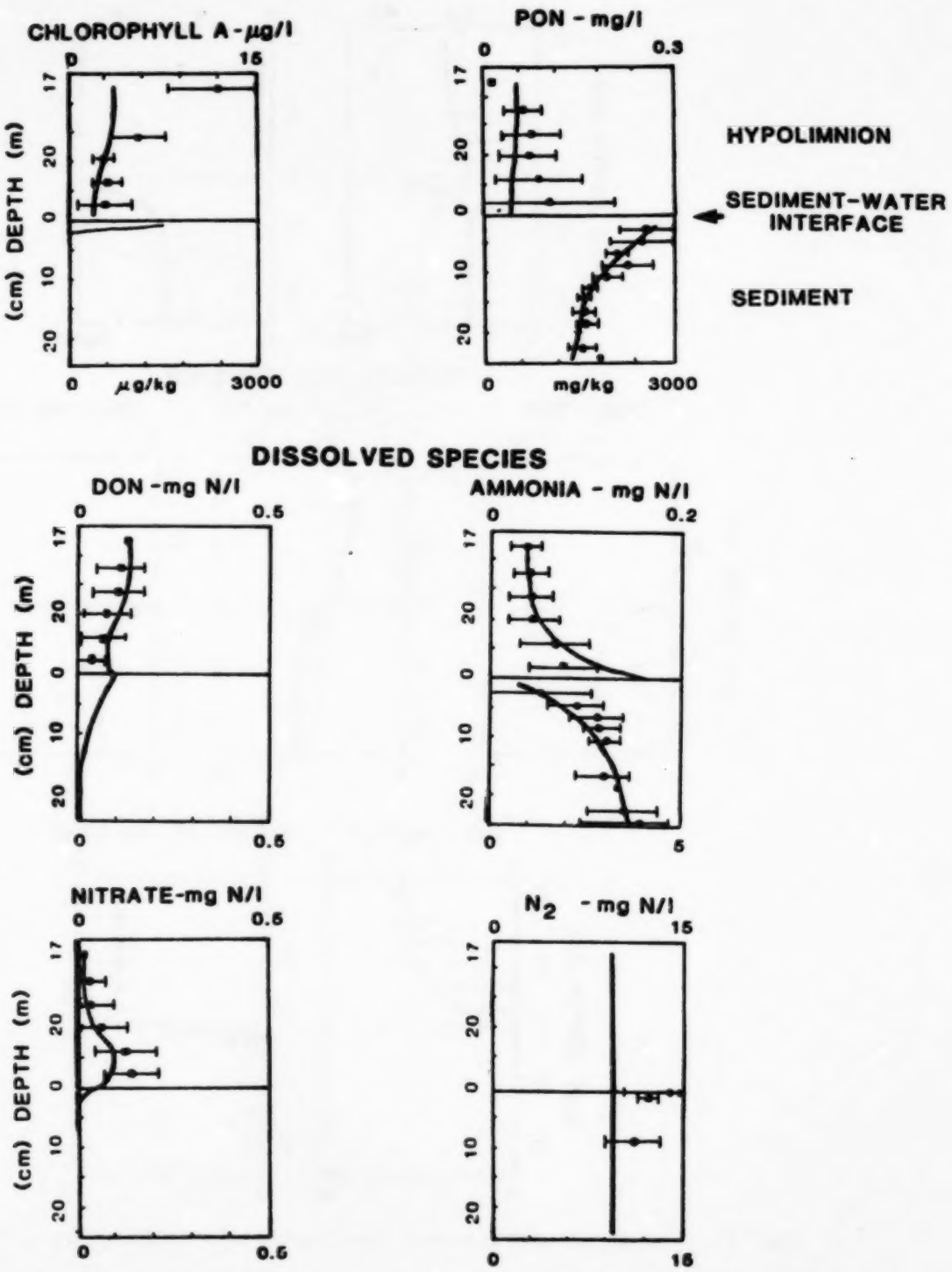


Fig. 10 Computed and observed hypolimnion and sediment distributions of nitrogen species.

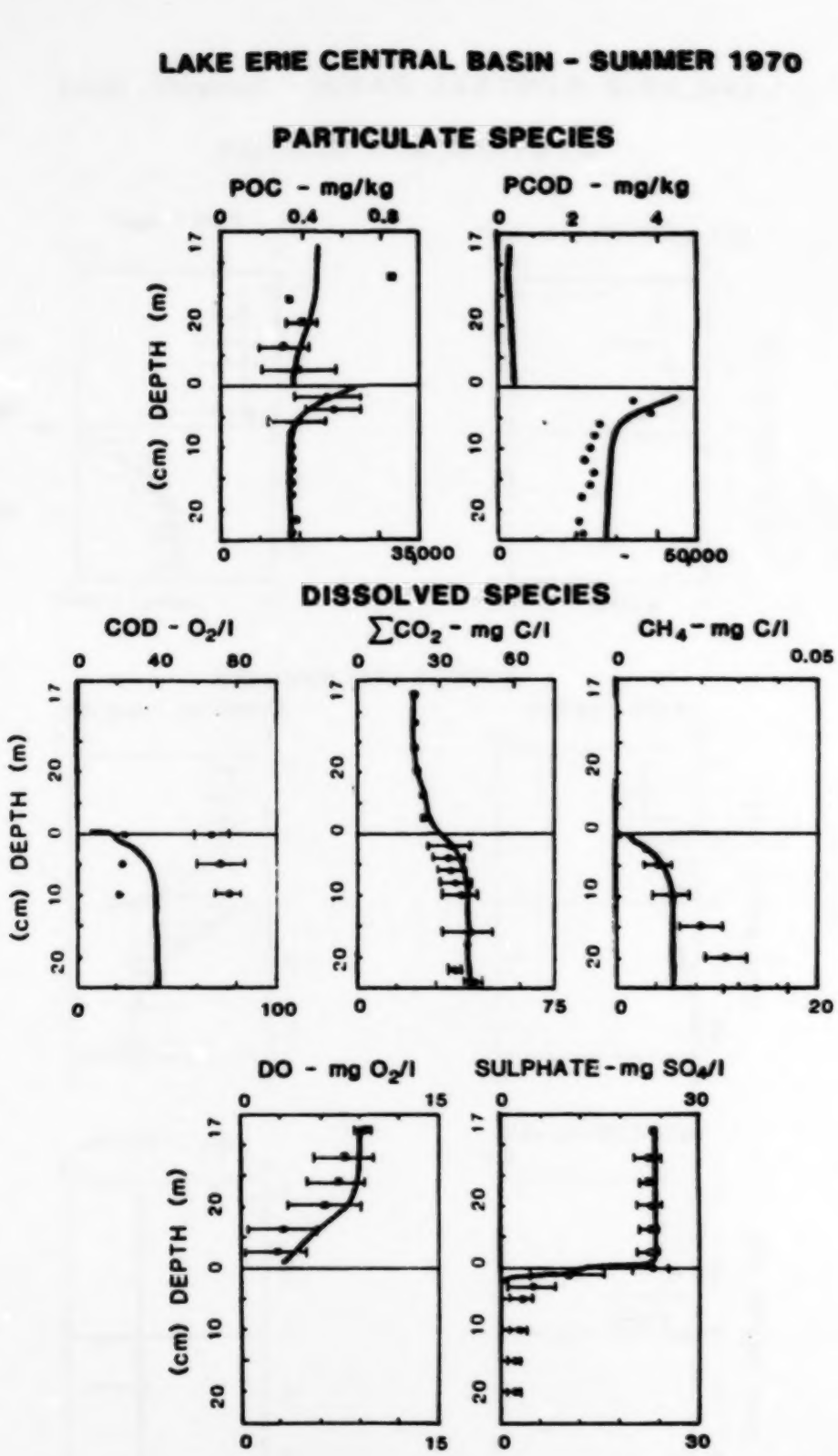


Fig. 11 Computed and observed hypolimnion and sediment distributions of organic and inorganic carbon species, oxygen and oxygen equivalents, and sulphate.

It is interesting to note that an attempt to quantify the individual components of the flux of reduced species to the sediment-water interface (Adams et al., 1982) accounted for only one-third of the measured SOD. It is probable that missing SOD is due to mineralization of labile particulate components at the interface and the presence of other reduced species. Unfortunately no COD concentrations or fluxes were measured.

It is interesting to note that the SOD predicted by eqs. (32) and (40) is quite close to the value obtained numerically. The flux of PCOD which reacts diagenetically is estimated from the hypolimnetic boundary concentration and aqueous settling velocity (w_a = 0.3 m/d) so that w_a [POC] = 122 mgC/m^2-d and J_{PCOD} = 326 mgO_2/m^2-d. The correction for burial is unimportant, $\eta >> 1$, and for denitrification: $[O_2]_o$ = 2 mg/ℓ and $[NO_3^-]_o$ = 0.33 mg N/ℓ so that the correction is 0.68 and $J_{O_2}^*$ = 222 mgO_2/m^2-d. Loss of solid phase oxygen equivalents can be estimated from sediment ferrous iron concentration ∿ 30 g Fe/kg so that $O_2^*(s) \sim -4.3$ g O_2/kg and w $O_2(s)$ = -19 mg O_2/m^2-d for a deep sedimentation velocity of w = 0.164 cm/yr. Thus the total SOD = 203 mg O_2/m -d. The denitrification correction is significant while the solid phase burial is less so.

Summary and Conclusions

The diagenetic oxygen equivalents model of SOD yield the following relationships. At thermodynamic equilibrium the SOD (= $J_{O_2(aq)}$) is equal to the flux of oxygen equivalents to the sediment water interface, which in turn is equal to the flux of dissolved COD from the interface.

$$J_{O_2(aq)} = J_{O_2}^* = -J_{COD} \tag{44}$$

The COD flux that actually oxidizes is the difference between the anaerobic and aerobic COD flux. To correct for this incomplete oxidation an empirical fraction, $f_{O_2}^*$, is introduced:

$$J_{O_2(aq)} = f_{O_2}^* J_{O_2}^* \tag{45}$$

where

$$f_{O_2}^* = \frac{J_{COD}|_{O_2=0} - J_{COD}|_{O_2>0}}{J_{COD}|_{O_2=0}} \tag{46}$$

Available data indicate that $f_{O_2}^* \sim 0.65 - 0.80$. The diagenetic equations predict that, at steady state:

$$J_{O_2}^* = \frac{\eta}{1+\eta} J_{PCOD} \tag{47}$$

where J_{PCOD} is the flux of diagenetically reactive particulate COD to the sediment. Available data (Table 1) indicate that the reactive fraction is ~ 0.5 for sediments. The correction due to burial of interstitial water and reduced solid phase formation is

$$J_{O_2}^* = J_{PCOD} + w[O_2^*]_\infty \tag{48}$$

where $[O_2^*]$ is the oxygen equivalents of the interstitial water and reduced inorganic solid phase. Alternately if J_{PCOD} is interpreted as the total (reactive + diagenetically inert) particulate COD, and $[O_2^*]_\infty$ is the total organic + inorganic bulk oxygen equivalents concentration then eq. (48) is simply a flux balance of total oxygen equivalents.

Corrections for the oxidation of diagenetically produced ammonia are likely to be small. Predicted effects of overlying water nitrate concentrations can be significant but are directly contradicted by experimental evidence that suggests no effect.

From the point of view of mechanisms, the principle factor is J_{PCOD}: the flux of diagenetically reactive particulate COD to the sediment. For steady state situations the reaction rate, diffusion coefficient and sedimentation velocity enter the calculation only as $\eta = KD/w^2$ and the correction just accounts for burial of interstitial water COD by sedimentation. Thus except for rare cases when η is not large, the steady state SOD is predicted to be independent of diffusion and reaction.

This suggests that the observed increases of SOD due to increased effects on stream velocity (Whittemore, 1983) or biological mixing of sediments are transitory, time variable phenomena. The increased surface mass transfer indeed causes an increased oxygen equivalents flux but this increased flux exceeds the rate of production of dissolved COD and eventually the interstitial O_2^* distribution readjusts so that the SOD is reduced to J_{PCOD}. From a mass balance point of view this conclusion is inescapable. Increased surface mass transfer does not increase the supply of PCOD to the sediment. Therefore the quantity of oxygen equivalents available to be exerted as SOD is fixed and cannot exceed the supply. The increased SOD observed at high stream velocities must be counterbalanced by a lower SOD during more quiescent periods so that the average SOD is equal to the average diagenetically reactive PCOD flux to the sediment. Increases in SOD due to the presence of benthic fauna may be attributable to a larger fraction of the total PCOD flux being reacted but the upper limit is again the flux of PCOD to the sediment.

The effect of overlying water dissolved oxygen concentration on SOD (e.g. Edwards and Rolley, 1965) can also be interpreted in light of the oxygen equivalents model. It is known that reducing overlying DO reduces the measured SOD flux. What appears to be occurring is that a portion

of the upward dissolved COD flux is escaping to the overlying water as unoxidized COD, i.e. $f_{O_2}^*$ is decreasing. Thus the overall oxygen demand of the sediment is not actually decreased. That fraction of J_{COD} which is not exerted at the sediment-water interface is transferred to the overlying water where it may react as a volumetric sink of DO. Whether it is a rapid or slow reaction is not clear. However it would be incorrect in dissolved oxygen models to reduce SOD at low DO concentrations and not also properly account for the unoxidized flux of interstitial water COD.

The division of SOD into chemical and biological components by inhibiting the bacteria actually examines the portion of the flux of oxygen equivalents that is oxidized at the interface either bacterially (presumably the organic carbon components) or chemically (the reduced Fe, Mn, and $S^=$ species) (Walker and Snodgrass, 1983). However it is clear that the source of SOD is sedimentary PCOD biological reactions. The fact that some of the oxidation occurs chemically at the interface is a consequence of the species distribution of electron acceptors that mediate the transport of oxygen equivalents that were biologically produced in the sediment.

With regard to laboratory measurements of SOD from either intact cores or grab samples of sediments, it is clear that the realism of the simulation of the field situation is directly related to either preserving the interstitial profile of oxygen equivalents, or allowing enough time to pass so that the profile is reestablished. For certain cases this time may be so long, since diagenetic reaction rates are slow (Table 1), that grab sample experiments are meaningless and only intact cores can be used. A clear distinction should be made between experiments

that are designed to measure the diagenesis and mineralization rates, and those that measure the flux of oxygen equivalents. The latter depend on preserving both the interstitial water oxygen equivalents concentration and duplicating the mass transport mechanisms in the measurement procedure.

The observations of SOD as a function of sediment depth can be interpreted in this light as well. The sludge incubation experiments of Fair et al. (1941) demonstrated an increasing SOD with increasing depth of sludge. Since the incubators were initially homogeneous it is reasonable to expect that the total production of COD(aq) was linearly increasing with depth, and if all the COD flux were oxidized at the interface then the SOD should be linearly increasing with depth in these experiments. A less than linear relationship was found and attributed to an increasing loss of methane to the overlying water. Thus $f_{O_2}^*$ was decreasing as sediment depth increased, producing the observed dependency.

By contrast Edwards and Rolley (1965) observed no depth effect and McDonnell and Hall (1969) observed a slight effect. Both these studies were based upon incubating intact cores. A depth dependency in this case would only be observed if (1) a significant portion of the diagenesis is occurring below the depth of the collected core and (2) if sufficient time elapses between collection and incubation so that the effect of the missing lower layers can diffuse to the interface. An estimate of this time is $t \sim \ell^2/4D$ so that short cores ($\sim$ 5 cm) could exhibit a reduced SOD if the time interval exceeded $\sim$ 10 days. However in most cases no depth effect should be observed.

The time variable behavior of SOD can be understood in terms of the time to steady state. For the fractions of PCOD that are mineralized at

reasonably rapid rates (~ 0.01/day) the SOD would respond to changes in PCOD loading within one year. However for the fraction due to the refractory component which mineralizes at slow diagenetic rates (Table 1) the response time for changes in PCOD loading is multiple years. Thus for practical purposes, it is essential that the fraction of SOD derived from labile and refractory components be quantified since only the former fraction will respond rapidly to loading changes.

Perhaps the most important consequence of the oxygen equivalents model of SOD is the implications with regard to field measurements and laboratory experiments. Direct measurements of aerobic and anaerobic COD fluxes together with SOD measurements give a direct check since mass balance of oxygen equivalents must apply. Direct measurements of interstitial water COD and NH_3 (the convenient tracer) together with estimates or measurements of the sediment-water mass transfer coefficient provide an additional framework for SOD estimates. Controlled laboratory experiments that are designed to further validate the predictions of the oxygen equivalents model are also necessary. The puzzling lack of an effect of overlying nitrate concentrations requires further investigation. The proposed model provides a framework for the design of these experiments and the evaluation of the results.

Further effort is also indicated with regard to integrating the oxygen equivalents model into conventional BOD-DO calculations. Field data sets which are suitable should either be located or generated so that fixed validation of these methods can proceed.

The oxygen equivalents model of SOD provides a simple, comprehensible framework within which to understand the phenomena of SOD. However it is certain that further refinements will be required as

these ideas are integrated into the practice of modeling dissolved oxygen in situations where SOD is an important component of the problem.

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